

We Claim:

1. A process for making an N-(phosphonomethyl)glycine product, the process comprising:
 - introducing an aqueous feed stream comprising an N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reactor system;
 - 5 oxidizing N-(phosphonomethyl)iminodiacetic acid substrate in the oxidation reactor system in the presence of an oxidation catalyst to produce a reaction product solution comprising N-(phosphonomethyl)glycine product;
 - dividing the reaction product solution into plural fractions comprising a primary fraction and a secondary fraction;
 - 10 precipitating N-(phosphonomethyl)glycine product crystals from the primary fraction to produce a primary product slurry comprising precipitated N-(phosphonomethyl)glycine product crystals and a primary mother liquor; and
 - precipitating N-(phosphonomethyl)glycine product crystals from an aqueous secondary crystallization feed mixture comprising N-(phosphonomethyl)glycine product contained in said secondary fraction to produce a secondary product slurry comprising precipitated N-(phosphonomethyl)glycine product crystals and a secondary mother liquor.
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2. The process as set forth in claim 1 wherein the primary fraction is cooled to precipitate N-(phosphonomethyl)glycine product crystals from the primary fraction and water is evaporated from the aqueous secondary crystallization feed mixture to precipitating N-(phosphonomethyl)glycine product crystals from the aqueous secondary crystallization feed mixture.
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3. The process as set forth in claim 2 wherein the primary fraction is cooled as water is evaporated from the primary fraction by reducing the pressure.

4. The process as set forth in claim 3 wherein water is evaporated from the primary fraction under substantially adiabatic conditions.
5. The process as set forth in claim 4 wherein the evaporation cools the primary fraction to a temperature of from about 45°C to about 80°C.
6. The process as set forth in claim 4 wherein from about 5% to about 30% by weight of the primary fraction is evaporated.
7. The process as set forth in claim 4 further comprising decanting primary mother liquor from the precipitated N-(phosphonomethyl)glycine product crystals in the primary product slurry.
8. The process as set forth in claim 7 further comprising recycling primary mother liquor decanted from the precipitated N-(phosphonomethyl)glycine product crystals in the primary product slurry to the oxidation reactor system for use as a source of process water.
9. The process as set forth in claim 8 wherein substantially all the primary mother liquor decanted from the precipitated N-(phosphonomethyl)glycine product crystals in the primary product slurry is recycled to the oxidation reactor system.
10. The process as set forth in claim 9 wherein the oxidation catalyst comprises a heterogenous catalyst comprising a noble metal deposited on a carbon support.
11. The process as set forth in claim 10 wherein the N-(phosphonomethyl)iminodiacetic acid substrate is oxidized in a liquid reaction

medium in contact with the oxidation catalyst and the chloride ion concentration in the liquid reaction medium is maintained at no greater than about 500 ppm by weight.

12. The process as set forth in claim 11 wherein the chloride ion concentration in the liquid reaction medium is maintained at no greater than 300 ppm by weight.

13. The process as set forth in claim 12 wherein the chloride ion concentration in the liquid reaction medium is maintained at no greater than 100 ppm by weight.

14. The process as set forth in claim 11 wherein a source of the N-(phosphonomethyl)iminodiacetic acid substrate is used to prepare the aqueous feed stream introduced into the reactor system and the concentration of chloride ion in the N-(phosphonomethyl)iminodiacetic acid substrate source is less than about 5000 ppm by weight on a dry basis.

15. The process as set forth in claim 14 wherein the concentration of chloride ion in the N-(phosphonomethyl)iminodiacetic acid substrate source is less than about 3000 ppm by weight on a dry basis.

16. The process as set forth in claim 15 wherein the concentration of chloride ion in the N-(phosphonomethyl)iminodiacetic acid substrate source is less than about 2000 ppm by weight on a dry basis.

17. The process as set forth in claim 16 wherein the concentration of chloride ion in the N-(phosphonomethyl)iminodiacetic acid substrate source is less than about 1000 ppm by weight on a dry basis.

18. The process as set forth in claim 4 wherein the process further comprises purging secondary mother liquor for removal of by-products and impurities from the process.

19. The process as set forth in claim 18 wherein substantially all the secondary mother liquor is purged from the process.

20. The process as set forth in claim 4 wherein the primary fraction is from about 30% to about 85% of the reaction product solution.

21. The process as set forth in claim 20 wherein the primary fraction is from about 50% to about 80% of the reaction product solution.

22. The process as set forth in claim 21 wherein the primary fraction is from about 65% to about 75% of the reaction product solution.

23. The process as set forth in claim 20 wherein the reactor system comprises a first and a second oxidation reaction zone in series;

the aqueous feed stream is introduced into the first oxidation reaction zone;

N-(phosphonomethyl)iminodiacetic acid substrate is continuously oxidized in

5 the first oxidation reaction zone to produce an intermediate reaction mixture comprising N-(phosphonomethyl)glycine product and unreacted N-(phosphonomethyl)iminodiacetic acid substrate;

an intermediate aqueous feed stream is introduced into the second oxidation reaction zone, the intermediate aqueous feed stream comprising N-

10 (phosphonomethyl)glycine product obtained in the intermediate reaction mixture and unreacted N-(phosphonomethyl)iminodiacetic acid substrate;

N-(phosphonomethyl)iminodiacetic acid substrate is continuously oxidized in the second oxidation reaction zone to produce the reaction product solution comprising N-(phosphonomethyl)glycine product; and

15 the reaction product solution is divided into plural fractions comprising the primary and secondary fractions.

24. The process as set forth in claim 23 wherein the oxidation catalyst is in contact with a liquid reaction medium in each of the oxidation reaction zones.

25. The process as set forth in claim 24 wherein the oxidation catalyst comprises a heterogenous particulate catalyst.

26. The process as set forth in claim 25 wherein the heterogeneous particulate catalyst comprises a noble metal deposited on a particulate carbon support.

27. The process of claim 4 wherein evaporative cooling of said primary fraction comprises:

 introducing an aqueous evaporation feed mixture into an evaporation zone, said aqueous feed mixture comprising said primary fraction;

5 evaporating water from said aqueous evaporation feed mixture in said evaporation zone in the presence of solid particulate N-(phosphonomethyl)glycine product, thereby producing a vapor phase comprising water vapor, precipitating N-(phosphonomethyl)glycine product from the aqueous liquid phase, and producing an evaporation product comprising N-(phosphonomethyl)glycine product solids and a 10 primary mother liquor that is substantially saturated or supersaturated in N-(phosphonomethyl)glycine product; and

 maintaining a ratio of particulate N-(phosphonomethyl)glycine product solids to primary mother liquor in said evaporation zone which exceeds the ratio of

15 N-(phosphonomethyl)glycine product solids incrementally produced by the effects of evaporation to mother liquor incrementally produced thereby.

28. The process as set forth in claim 27 wherein said evaporation product is divided to provide an N-(phosphonomethyl)glycine product solids fraction that is relatively depleted in mother liquor and a primary mother liquor fraction that is relatively depleted in N-(phosphonomethyl)glycine product solids.

29. The process as set forth in claim 28 wherein maintaining said ratio of particulate N-(phosphonomethyl)glycine product solids to mother liquor in said evaporation zone comprises returning solids obtained in said solids fraction to said evaporation zone or retaining solids obtained in said solid fraction within said zone.

30. The process as set forth in claim 29 comprising:

introducing an evaporation feed mixture comprising said primary fraction into a vapor/liquid separation zone of said evaporation zone wherein the pressure is below the vapor pressure of said mixture, thereby allowing water to flash from the evaporation feed mixture, producing a vapor phase comprising water vapor, and precipitating N-(phosphonomethyl)glycine product from the liquid phase to produce a first slurry stream comprising particulate N-(phosphonomethyl)glycine product in a saturated or supersaturated mother liquor;

separating said vapor phase from said first slurry stream;

10 introducing said first slurry stream into a retention zone in which a supernatant liquid comprising a fraction of said mother liquor is separated from a second slurry stream comprising precipitated N-(phosphonomethyl)glycine product and mother liquor, said retention zone having an inlet for said first slurry, a decantation liquid exit for said supernatant liquid spaced above said inlet, and an exit for said second slurry spaced above said inlet but below said decantation liquid exit; and

maintaining the relative rates at which said first slurry is introduced into said retention zone, said second slurry is drawn off through said second slurry exit and said supernatant liquid is drawn off through said decantation liquid exit such that the upward flow velocity in a lower region of said retention zone below said second slurry exit is sufficient to maintain precipitated N-(phosphonomethyl)glycine product in suspension in the liquid phase while the upward flow velocity in an upper region of said retention zone above said second slurry exit is below the sedimentation velocity of at least 80% by weight of the N-(phosphonomethyl)glycine product particles in said lower region.

20 31. The process as set forth in claim 30 wherein at least a portion of said second slurry stream is recirculated to said vapor/liquid separation zone.

32. The process as set forth in claim 31 wherein at least a portion of said second slurry stream and said primary fraction together comprise the evaporation feed mixture introduced into said vapor/liquid separation zone.

33. The process as set forth in claim 32 wherein a third slurry stream is removed from said lower region of said zone.

34. The process as set forth in claim 33 wherein the relative rates of the flow of said primary fraction to said vapor/liquid separation zone, recirculation of all or part of said second slurry stream to said vapor/liquid separation zone, withdrawal of said supernatant liquid from said decantation liquid exit, withdrawal of said third slurry stream from said lower region of said retention zone, and return to said evaporation zone of any liquid or solids bearing streams from any solids/liquid separations to which said third slurry may be subjected, are sufficient to establish a ratio of N-(phosphonomethyl)glycine product solids to mother liquor in said lower region of said zone that is higher than the ratio of precipitated solid

- 10 N-(phosphonomethyl)glycine product incrementally produced by the effects of evaporation of said primary fraction to mother liquor incrementally produced thereby.

35. The process as set forth in claim 34 wherein the relative flow rates of said streams are controlled so that the N-(phosphonomethyl)glycine product solids concentration in said lower region of said zone is at least about twice the concentration of N-(phosphonomethyl)glycine product solids in the mixture of such 5 solids and mother liquor that is or would be produced by flashing of said primary fraction in said vapor/liquid zone in the absence of said recirculated second slurry stream.

36. The process as set forth in claim 35 wherein solids are removed from said third slurry to produce a recycle liquid fraction which is recirculated to said vapor/liquid separation zone, whereby said evaporation feed mixture further comprises said recycle liquid fraction.

37. The process as set forth in claim 36 wherein both said primary fraction and said recycle liquid fraction are mixed with said second slurry stream prior to introduction into said vapor/liquid separation zone.

38. The process as set forth in claim 37 wherein said secondary fraction is introduced into a secondary reactor system comprising a tertiary oxidation reaction zone, unreacted N-(phosphonomethyl)iminodiacetic acid substrate contained in said secondary fraction being converted to N-(phosphonomethyl)glycine product in said 5 tertiary oxidation reaction zone to produce a tertiary oxidation reaction mixture, said secondary crystallization feed mixture comprising N-(phosphonomethyl)glycine product contained in said tertiary oxidation reaction mixture.

39. The process as set forth in claim 37 wherein the relative flow rates of all of said streams, including said recycle liquid fraction, are controlled so that the solids content of the slurry in said lower region of said zone is at least about 12% by weight.

40. The process as set forth in claim 39 further comprising decanting primary mother liquor from the precipitated N-(phosphonomethyl)glycine product crystals in the primary product slurry.

41. The process as set forth in claim 39 further comprising recycling primary mother liquor to said oxidation reactor system for use as a source of water.

42. The process as set forth in claim 39 further comprising purging secondary mother liquor for removal of by-products and impurities from the process.

43. The process as set forth in claim 39 wherein said oxidation reactor system comprises a series of at least two continuous oxidation reaction zones, the process further comprising:

separating the oxidation catalyst from reaction product solution; and

5 continuously recycling the separated oxidation catalyst to at least one of the oxidation reaction zones.

44. A process for making an N-(phosphonomethyl)glycine product, the process comprising:

introducing an aqueous feed stream comprising an N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reactor system;

5 oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate in the oxidation reactor system in the presence of an oxidation catalyst to produce a reaction product solution containing N-(phosphonomethyl)glycine product;

precipitating N-(phosphonomethyl)glycine product crystals from the reaction product solution to produce a primary product slurry comprising precipitated N-(phosphonomethyl)glycine product crystals and a primary mother liquor; and

10 evaporating water from the primary mother liquor, thereby precipitating additional N-(phosphonomethyl)glycine product crystals and producing a secondary mother liquor.

45. The process as set forth in claim 44 wherein the reaction product solution is cooled to precipitate N-(phosphonomethyl)glycine product crystals from the reaction product solution.

46. The process as set forth in claim 45 wherein the reaction product solution is cooled as water is evaporated from the reaction product solution by reducing the pressure.

47. The process as set forth in claim 46 wherein water is evaporated from the reaction product solution under substantially adiabatic conditions.

48. The process as set forth in claim 47 wherein the evaporation cools the reaction product solution to a temperature of from about 45°C to about 80°C.

49. The process as set forth in claim 47 wherein from about 5% to about 30% by weight of the reaction product solution is evaporated.

50. The process as set forth in claim 47 wherein the process further comprises purging secondary mother liquor for removal of by-products and impurities from the process.

51. The process as set forth in claim 50 wherein substantially all the secondary mother liquor is purged from the process.

52. A process for making an N-(phosphonomethyl)glycine product, the process comprising:

- introducing an aqueous feed stream comprising an N-(phosphonomethyl)iminodiacetic acid substrate into a primary oxidation reactor system comprising one or more oxidation reaction zones;
- 5 oxidizing N-(phosphonomethyl)iminodiacetic acid substrate in the primary oxidation reactor system to produce a reaction product solution comprising N-(phosphonomethyl)glycine product and unreacted N-(phosphonomethyl)iminodiacetic acid substrate;
- 10 dividing the reaction product solution into plural fractions comprising a primary fraction and a secondary oxidation reactor feed fraction;
- precipitating N-(phosphonomethyl)glycine product crystals from the primary fraction to produce a primary product slurry comprising precipitated N-(phosphonomethyl)glycine product crystals and a primary mother liquor;
- 15 introducing the secondary oxidation reactor feed fraction into a secondary oxidation reactor system comprising one or more oxidation reaction zones;
- oxidizing N-(phosphonomethyl)iminodiacetic acid substrate in the secondary oxidation reactor system to produce a secondary oxidation reactor effluent comprising N-(phosphonomethyl)glycine product; and
- 20 precipitating N-(phosphonomethyl)glycine product crystals from the secondary oxidation reactor effluent to produce a secondary product slurry comprising precipitated N-(phosphonomethyl)glycine product crystals and a secondary mother liquor.

53. The process as set forth in claim 52 wherein the primary fraction is cooled to precipitate N-(phosphonomethyl)glycine product crystals from the primary fraction

and water is evaporated from the secondary oxidation reactor effluent to precipitate N-(phosphonomethyl)glycine product crystals from the secondary oxidation reactor
5 effluent.

54. The process as set forth in claim 53 wherein the primary fraction is cooled as water is evaporated from the primary fraction by reducing the pressure.

55. The process as set forth in claim 54 wherein the water is evaporated from the primary fraction under substantially adiabatic conditions.

56. The process as set forth in claim 52 wherein the primary reactor system comprises multiple oxidation reaction zones in series.

57. The process as set forth in claim 56 wherein the reaction product solution is divided after the last oxidation reaction zone in the series.

58. The process as set forth in claim 56 wherein the reaction product solution is divided before the last oxidation reaction zone in the series and the primary fraction passes through at least one further oxidation reaction zone in the primary reactor system before precipitating N-(phosphonomethyl)glycine product crystals from the
5 primary fraction.

59. The process as set forth in claim 52 wherein the primary reactor system comprises a single oxidation reaction zone.

60. The process as set forth in claim 52 wherein the secondary oxidation reactor system comprises a stirred tank reactor.

61. The process as set forth in claim 52 wherein the secondary oxidation reactor system comprises a fixed bed reactor.
62. The process as set forth in claim 61 wherein the fixed bed reactor is operated with cocurrent gas and liquid flows through the oxidation reaction zone.
63. The process as set forth in claim 61 wherein the fixed bed reactor is operated adiabatically.
64. The process as set forth in claim 52 wherein the secondary oxidation feed fraction is cooled prior to introduction into the secondary oxidation reactor system.
65. A process for preparing an N-(phosphonomethyl)glycine product by oxidizing an N-(phosphonomethyl)iminodiacetic acid substrate, the process comprising:
introducing the N-(phosphonomethyl)iminodiacetic acid substrate into a liquid reaction medium within an oxidation reaction zone, the oxidation reaction zone being substantially back-mixed in the liquid phase and containing a catalyst for the oxidation reaction in contact with the liquid reaction medium, the liquid reaction medium comprising the N-(phosphonomethyl)glycine product;
introducing an oxidizing agent into the oxidation reaction zone;
continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate in the oxidation reaction zone to form the N-(phosphonomethyl)glycine product; and
continuously withdrawing a reaction mixture effluent comprising the N-(phosphonomethyl)glycine product from the oxidation reaction zone.
66. The process as set forth in claim 65 wherein the catalyst comprises a heterogeneous particulate catalyst suspended in the liquid reaction medium within the

oxidation reaction zone, the catalyst comprising a noble metal deposited on a particulate carbon support.

67. The process as set forth in claim 66 wherein the oxidation reaction zone is provided by an ejector nozzle loop reactor.

68. The process as set forth in claim 67 wherein the oxidizing agent is an O₂-containing gas and is introduced simultaneously with the aqueous feed stream into the oxidation reaction zone through an ejector nozzle of the ejector nozzle loop reactor.

69. The process is set forth in claim 66 wherein the oxidation reaction zone is provided by a fluidized bed reactor.

70. The process as set forth in claim 66 wherein the oxidation reaction zone is provided by a continuous stirred tank reactor.

71. The process as set forth in claim 70 wherein the particulate carbon support exhibits a particle size distribution such that about 95% of the catalyst particles are from about 3 to about 100 µm in their largest dimension.

72. The process as set forth in claim 71 wherein the average particle size of the particulate catalyst is from about 15 to about 40 µm.

73. The process as set forth in claim 71 wherein the concentration of the particulate catalyst within the oxidation reaction zone is from about 0.1 to about 10 wt.% based on the total weight of catalyst and the liquid reaction medium in the oxidation reaction zone.

74. The process as set forth in claim 70 further comprising cooling the liquid reaction medium.

75. The process as set forth in claim 74 wherein the liquid reaction medium is cooled in an external heat transfer recirculation loop comprising a heat exchanger.

76. The process as set forth in claim 70 wherein the oxidizing agent is an O₂-containing gas and is sparged into the liquid reaction medium within the oxidation reaction zone.

77. The process as set in claim 70 wherein the reaction mixture effluent withdrawn from the oxidation reaction zone is substantially free of the particulate catalyst, the stirred tank reactor comprising an internal catalyst filter for preventing the particulate catalyst from being withdrawn from the oxidation reaction zone with 5 the reaction mixture effluent.

78. The process as set forth in claim 70 wherein the reaction mixture effluent withdrawn from the oxidation reaction zone further comprises the particulate catalyst, the process further comprising:

separating the particulate catalyst from the reaction mixture effluent to form a 5 catalyst recycle stream comprising the separated particulate catalyst; and

introducing at least a portion of the particulate catalyst contained in the catalyst recycle stream into the oxidation reaction zone.

79. The process as set forth in claim 78 wherein catalyst is purged from the catalyst recycle stream.

80. The process as set forth in claim 79 wherein fresh catalyst is added to the catalyst recycle stream.

81. The process as set forth in claim 78 wherein the particulate catalyst is separated from the reaction mixture effluent in a catalyst filter to form the catalyst recycle stream and a filtrate substantially free of the particulate catalyst and comprising the N-(phosphonomethyl)glycine product.

82. The process as set forth in claim 81 wherein the catalyst filter is adapted for continuous separation of particulate catalyst from the reaction mixture effluent.

83. The process as set forth in claim 82 wherein the catalyst filter is a continuous cross-flow filter.

84. The process as set forth in claim 82 wherein the catalyst filter is a continuous back-pulse filter.

85. The process as set forth in claim 84 wherein the back-pulse filter comprises a filter element and a portion of the filtrate is used to back-pulse the filter element and remove separated catalyst from the filter element.

86. The process as set forth in claim 84 wherein the reaction mixture effluent further comprises dissolved CO₂, the reaction mixture effluent being passed through a flash tank before being introduced into the catalyst filter to lower the pressure on the reaction mixture effluent and remove dissolved CO₂ from the reaction mixture effluent.

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87. The process as set forth in claim 84 wherein at least a portion of the particulate catalyst contained in the catalyst recycle stream passes through a catalyst holding tank before being introduced into the oxidation reaction zone.

88. The process as set forth in claim 87 wherein the catalyst holding tank is substantially free of O₂.

89. The process as set forth in claim 88 further comprising introducing a non-oxidizing gas into the catalyst holding tank.

90. The process as set forth in claim 88 wherein the residence time of the recycled catalyst in the catalyst holding tank is at least about 2 minutes.

91. The process as set forth in claim 81 wherein the filtrate comprises unreacted N-(phosphonomethyl)iminodiacetic acid substrate, the process further comprising:

continuously introducing the filtrate into a second oxidation reaction zone;
5 introducing an oxidizing agent into the second oxidation reaction zone; and
 continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate in the second oxidation reaction zone to form additional N-(phosphonomethyl)glycine product.

92. The process as set forth in claim 91 wherein the second oxidation reaction zone is substantially back-mixed in the liquid phase.

93. The process as set forth in claim 92 wherein the second oxidation reaction zone is provided by a second stirred tank reactor.

94. The process as set forth in claim 92 wherein the second oxidation reaction zone is provided by an ejector nozzle loop reactor.

95. The process as set forth in claim 91 wherein the second oxidation reaction zone is provided by a fixed bed reactor.

96. A process for preparing an N-(phosphonomethyl)glycine product by oxidizing an N-(phosphonomethyl)iminodiacetic acid substrate, the process comprising:

- introducing the N-(phosphonomethyl)iminodiacetic acid substrate into a liquid reaction medium within an oxidation reaction zone, the liquid reaction medium comprising the N-(phosphonomethyl)glycine product and having a particulate heterogeneous catalyst for the oxidation reaction suspended therein;
- 5 introducing an oxidizing agent into the oxidation reaction zone;
- continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate in the liquid reaction medium within the oxidation reaction zone to form the N-(phosphonomethyl)glycine product;
- 10 continuously withdrawing a reaction mixture effluent from said oxidation reaction zone, the reaction mixture effluent comprising the N-(phosphonomethyl)glycine product;
- continuously withdrawing a reaction mixture effluent from said oxidation reaction zone, the reaction mixture effluent comprising the N-(phosphonomethyl)glycine product;
- 15 continuously separating the particulate catalyst from the reaction mixture effluent to form a catalyst recycle stream comprising the separated catalyst; and
- introducing at least a portion of the particulate catalyst contained in the catalyst recycle stream into said oxidation reaction zone.

97. The process as set forth in claim 96 wherein particulate catalyst contained in the catalyst recycle stream passes through at least one other oxidation reaction zone before being introduced into said oxidation reaction zone.

98. The process as set forth in claim 96 wherein particulate catalyst contained in the catalyst recycle stream is introduced directly into said oxidation reaction zone.

99. The process as set forth in claim 96 wherein the particulate catalyst is separated from the reaction mixture effluent in a catalyst filter to form the catalyst

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recycle stream and a filtrate substantially free of the particulate catalyst and comprising N-(phosphonomethyl)glycine product.

100. The process as set forth in claim 99 wherein the catalyst filter is adapted for continuous separation of the particulate catalyst from the reaction mixture effluent.

101. A process for preparing an N-(phosphonomethyl)glycine product by oxidizing an N-(phosphonomethyl)iminodiacetic acid substrate in a reactor system, the process comprising:

- introducing an aqueous feed stream comprising the N-
- 5 (phosphonomethyl)iminodiacetic acid substrate into a first oxidation reaction zone;
- introducing an oxidizing agent into the first oxidation reaction zone;
- continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate in the first oxidation reaction zone to form the N-(phosphonomethyl)glycine product;
- continuously withdrawing an intermediate reaction mixture effluent
- 10 comprising the N-(phosphonomethyl)glycine product and unreacted N-(phosphonomethyl)iminodiacetic acid substrate from the first oxidation reaction zone;
- continuously introducing an intermediate aqueous feed stream into a second oxidation reaction zone, the intermediate aqueous feed stream comprising N-(phosphonomethyl)glycine product and unreacted N-(phosphonomethyl)iminodiacetic acid substrate obtained in the intermediate reaction mixture effluent;
- 15 introducing an oxidizing agent into the second oxidation reaction zone;
- continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate in the second oxidation reaction zone to form additional N-(phosphonomethyl)glycine product; and
- 20 continuously withdrawing a reaction mixture effluent comprising the N-(phosphonomethyl)glycine product from the second oxidation reaction zone.

102. The process as set forth in claim 101 wherein the first and second oxidation reaction zones contain a catalyst for the oxidation reaction.

103. The process as set forth in claim 102 wherein the catalyst in the first oxidation reaction zone is a heterogeneous particulate catalyst and is suspended in a liquid reaction medium comprising the N-(phosphonomethyl)iminodiacetic acid substrate.

104. The process as set forth in claim 103 wherein the first oxidation reaction zone is substantially back-mixed in the liquid phase.

105. The process as set forth in claim 104 wherein the first oxidation reaction zone is provided by a stirred tank reactor.

106. The process as set forth in claim 104 wherein the first oxidation reaction zone is provided by an ejector nozzle loop reactor.

107. The process as set forth in claim 104 wherein the first oxidation reaction zone is provided by a fluidized bed reactor.

108. The process as set forth in claim 104 wherein the second oxidation reaction zone is provided by a fixed bed having the catalyst therein.

109. The process as set forth in claim 102 wherein the catalyst in the first and second oxidation reaction zones is a heterogeneous particulate catalyst and is suspended in a liquid reaction medium comprising the N-(phosphonomethyl)iminodiacetic acid substrate.

110. The process as set forth in claim 109 wherein the first and second oxidation reaction zones are substantially back-mixed in the liquid phase.

111. The process as set forth in claim 110 wherein the oxidizing agent introduced into the first and second oxidation reaction zones is an O₂-containing gas and the second oxidation reaction zone is substantially back-mixed in the gas phase.

112. The process as set forth in claim 111 wherein the first and second oxidation reaction zones are provided by first and second continuous stirred tank reactors respectively, the stirred tank reactors containing a headspace above the liquid reaction medium and the second stirred tank reactor being provided with an impeller system adapted to draw gas from the headspace into the liquid reaction medium.
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113. The process as set forth in claim 112 wherein the O₂-containing gas is introduced into the headspace above the liquid reaction medium within the second stirred tank reactor.

114. The process as set forth in claim 111 wherein the first oxidation reaction zone is provided by a continuous stirred tank reactor and the second oxidation reaction zone is provided by an ejector nozzle loop reactor.

115. The process as set forth in claim 110 wherein the first and second oxidation reaction zones are provided by first and second continuous stirred tank reactors respectively.

116. The process as set forth in claim 115 wherein the heterogeneous particulate catalyst comprises a noble metal deposited on a particulate carbon support.

117. The process as set forth in claim 116 wherein the particulate carbon support exhibits a particle size distribution such that about 95% of the catalyst particles are from about 3 to about 100 μm in their largest dimension.
118. The process as set forth in claim 117 wherein the average particle size of the particulate catalyst is from about 15 to about 40 μm .

119. The process as set forth in claim 117 wherein the concentration of the particulate catalyst within the first and second oxidation reaction zones is from about 0.1 to about 10 wt.% based on the total weight of catalyst and the liquid reaction medium in the oxidation reaction zones.

120. The process as set forth in claim 119 wherein the reaction mixture effluent withdrawn from the second oxidation reaction zone further comprises the particulate catalyst, the process further comprising separating the particulate catalyst from the reaction mixture effluent withdrawn from the second oxidation reaction zone 5 to form a catalyst recycle stream comprising the separated catalyst.

121. The process as set forth in claim 120 further comprising introducing at least a portion of the particulate catalyst contained in the catalyst recycle stream into at least one of the first and second oxidation reaction zones.

122. The process as set forth in claim 121 wherein the particulate catalyst is separated from the reaction mixture effluent in a catalyst filter to form the catalyst recycle stream and a filtrate substantially free of the particulate catalyst and comprising the N-(phosphonomethyl)glycine product.

123. The process as set forth in claim 122 wherein the catalyst filter is adapted for continuous separation of particulate catalyst from the reaction mixture effluent.

124. The process as set forth in claim 123 wherein the catalyst filter is a continuous back-pulse filter.

125. The process as set forth in claim 124 wherein the back-pulse filter comprises a filter element and a portion of the filtrate is used to back-pulse the filter element and remove separated catalyst from the filter element.

126. The process as set forth in claim 124 wherein at least a portion of the particulate catalyst contained in the catalyst recycle stream passes through a catalyst holding tank before being introduced into at least one of the first and second oxidation reaction zones.

127. The process as set forth in claim 126 wherein the catalyst holding tank is substantially free of O₂.

128. The process as set forth in claim 127 further comprising introducing a non-oxidizing gas into the catalyst holding tank.

129. The process as set forth in claim 127 wherein the residence time of the recycled catalyst in the catalyst holding tank is at least about 2 minutes.

130. The process as set forth in claim 121 wherein at least a portion of the particulate catalyst contained in the catalyst recycle stream is introduced into the first oxidation reaction zone concurrently with the N-(phosphonomethyl)iminodiacetic acid substrate.

131. The process as set forth in claim 121 wherein at least a portion of the particulate catalyst contained in the catalyst recycle stream is introduced into the second oxidation reaction zone concurrently with the unreacted N-(phosphonomethyl)iminodiacetic acid substrate obtained in the intermediate aqueous 5 reaction mixture effluent.

132. The process as set forth in claim 121 wherein a portion of the particulate catalyst contained in the catalyst recycle stream is introduced into the first oxidation reaction zone concurrently with the N-(phosphonomethyl)iminodiacetic acid substrate and another portion of the particulate catalyst contained in the catalyst recycle stream 5 is introduced into the second oxidation reaction zone concurrently with the unreacted N-(phosphonomethyl)iminodiacetic acid substrate obtained in the intermediate aqueous reaction mixture effluent.

133. The process as set forth in claim 121 wherein catalyst is purged from the catalyst recycle stream.

134. The process as set forth in claim 133 wherein fresh catalyst is added to the catalyst recycle stream.

135. The process as set forth in claim 119 wherein the intermediate reaction mixture effluent withdrawn from the first oxidation reaction zone further comprises the particulate catalyst.

136. The process as set forth in claim 135 wherein the intermediate aqueous feed stream introduced into the second oxidation reaction zone further comprises particulate catalyst obtained in the intermediate reaction mixture effluent.

137. The process as set forth in claim 135 further comprising:

separating the particulate catalyst from the intermediate reaction mixture effluent withdrawn from the first oxidation reaction zone to form a catalyst recycle stream comprising the separated catalyst; and

- 5 introducing at least a portion of the particulate catalyst contained in the catalyst recycle stream into the first oxidation reaction zone concurrently with the N-(phosphonomethyl)iminodiacetic acid substrate.

138. The process as set forth in claim 137 wherein the particulate catalyst is separated from the intermediate reaction mixture effluent in a catalyst filter to form the catalyst recycle stream and a filtrate substantially free of the particulate catalyst and comprising the N-(phosphonomethyl)glycine product and the intermediate aqueous feed stream introduced into the second oxidation reaction zone comprises the filtrate.

- 5 139. The process as set forth in claim 138 wherein the reaction mixture effluent withdrawn from the second oxidation reaction zone further comprises the particulate catalyst, the process further comprising separating the particulate catalyst from the reaction mixture effluent withdrawn from the second oxidation reaction zone to form a second catalyst recycle stream comprising the separated catalyst.

140. The process as set forth in claim 139 wherein the particulate catalyst is separated from the reaction mixture effluent in a second catalyst filter to form the second catalyst recycle stream and a second filtrate substantially free of the particulate catalyst and comprising the N-(phosphonomethyl)glycine product.

141. The process as set forth in claim 140 further comprising introducing at least a portion of the particulate catalyst contained in the second catalyst recycle stream into at least one of the first and second oxidation reaction zones.

142. The process as set forth in claim 141 wherein at least a portion of the particulate catalyst contained in the second catalyst recycle stream is introduced into the second oxidation reaction zone concurrently with the unreacted N-(phosphonomethyl)iminodiacetic acid substrate obtained in the intermediate reaction

5 mixture effluent.

143. The process as set forth in claim 142 wherein the average age of the catalyst in the first oxidation reaction zone is different from the average age of the catalyst in the second oxidation reaction zone.

144. The process as set forth in claim 143 wherein the average age of the catalyst in the first oxidation reaction zone is greater than the average age of the catalyst in the second oxidation reaction zone.

145. The process as set forth in claim 143 wherein the average age of the catalyst in the first oxidation reaction zone is less than the average age of the catalyst in the second oxidation reaction zone.

146. The process as set forth in claim 140 wherein the catalyst filters are adapted for continuous separation of particulate catalyst from the intermediate reaction mixture effluent and the reaction mixture effluent.

147. The process as set forth in claim 119 further comprising cooling the liquid reaction medium in the first oxidation reaction zone.

148. The process as set forth in claim 147 wherein the liquid reaction medium in the first oxidation reaction zone is cooled in an external heat transfer recirculation loop comprising a heat exchanger associated with the first stirred tank reactor.

149. The process as set forth in claim 147 wherein the second oxidation reaction zone is operated adiabatically.

150. The process as set forth in claim 147 further comprising cooling the liquid reaction medium in the second oxidation reaction zone.

151. The process as set forth in claim 150 wherein the liquid reaction medium in the second oxidation reaction zone is cooled in an external heat transfer recirculation loop comprising a heat exchanger associated with the second stirred tank reactor.

152. The process as set forth in claim 150 wherein the temperature of the liquid reaction medium in the first oxidation reaction zone is maintained at from about 95°C to about 105°C and the temperature of the liquid reaction medium in the second oxidation reaction zone is maintained at from about 100°C to about 105°C.

153. The process as set forth in claim 119 wherein the concentration of the N-(phosphonomethyl)iminodiacetic acid substrate in the aqueous feed stream is from about 7% to about 15% by weight.

154. The process as set forth in claim 153 wherein the oxidizing agent is an O₂-containing gas and the O₂-containing gas is sparged into the liquid reaction medium within the first and second oxidation reaction zones.

155. The process as set forth in claim 154 wherein the total oxygen introduced into the first and second oxidation reaction zones combined is from about 0.5 to about 5 moles of O₂ per mole of N-(phosphonomethyl)iminodiacetic acid substrate in the aqueous feed stream introduced into the first stirred tank reactor.

156. The process as set forth in claim 155 wherein the total oxygen introduced into the first and second oxidation reaction zones combined is from about 1 to about 3 moles of O₂ per mole of N-(phosphonomethyl)iminodiacetic acid substrate in the aqueous feed stream introduced into the first stirred tank reactor.

157. The process as set forth in claim 156 wherein the total oxygen introduced into the first and second oxidation reaction zones combined is from about 1.5 to about 2.5 moles of O₂ per mole of N-(phosphonomethyl)iminodiacetic acid substrate in the aqueous feed stream introduced into the first stirred tank reactor.

158. The process as set forth in claim 156 wherein the N-(phosphonomethyl)iminodiacetic acid substrate concentration in the reaction mixture effluent withdrawn from the second stirred tank reactor is from about 200 to about 2000 ppm by weight.

159. The process as set forth in claim 158 wherein the N-(phosphonomethyl)iminodiacetic acid substrate concentration in the reaction mixture effluent withdrawn from the second stirred tank reactor is from about 500 to about 1500 ppm by weight.

160. The process as set forth in claim 159 wherein the N-(phosphonomethyl)iminodiacetic acid substrate concentration in the reaction mixture effluent withdrawn from the second stirred tank reactor is from about 500 to about 700 ppm by weight.

161. The process as set forth in claim 156 wherein the conversion of the N-(phosphonomethyl)iminodiacetic acid substrate to N-(phosphonomethyl)glycine product in the first oxidation reaction zone is at least about 70%.

162. The process as set forth in claim 161 wherein the conversion of the N-(phosphonomethyl)iminodiacetic acid substrate to N-(phosphonomethyl)glycine product in the first oxidation reaction zone is from about 80% to about 95%.

163. The process as set forth in claim 162 wherein from about 70% to about 90% of the total oxygen introduced into the first and second oxidation reaction zones is introduced into the first stirred tank reactor.

164. The process as set forth in claim 154 wherein the O₂-containing gas is introduced into the first oxidation reaction zone at a rate such that at least about 60% of the O₂ is utilized in the first oxidation reaction zone.

165. The process as set forth in claim 164 wherein the O₂-containing gas is introduced into the first oxidation reaction zone at a rate such that at least about 80% of the O₂ is utilized in the first oxidation reaction zone.

166. The process as set forth in claim 165 wherein the O₂-containing gas is introduced into the first oxidation reaction zone at a rate such that at least about 90% of the O₂ is utilized in the first oxidation reaction zone.

167. The process as set forth in claim 154 wherein the O₂-containing gas is introduced into the second oxidation reaction zone at a rate such that at least about 60% of the O₂ is utilized in the second oxidation reaction zone.

168. The process as set forth in claim 167 wherein the O₂-containing gas is introduced into the second oxidation reaction zone at a rate such that at least about 80% of the O₂ is utilized in the second oxidation reaction zone.

169. The process as set forth in claim 168 wherein the O₂-containing gas is introduced into the second oxidation reaction zone at a rate such that at least about 90% of the O₂ is utilized in the second oxidation reaction zone.

170. The process as set forth in claim 119 wherein the ratio of the working volume of liquid reaction medium in the first stirred tank reactor to the working volume of liquid reaction medium in the second stirred tank reactor is greater than 1.

171. The process as set forth in claim 170 wherein the ratio of the working volume of liquid reaction medium in the first stirred tank reactor to the working volume of liquid reaction medium in the second stirred tank reactor is from about 1.1 to about 5.

172. The process as set forth in claim 119 wherein the residence time in the first stirred tank reactor is from about 10 to about 30 minutes.

173. The process as set forth in claim 172 wherein the residence time in the second stirred tank reactor is from about 6 to about 20 minutes.

174. The process as set forth in claim 119 wherein the particulate catalyst further comprises a catalyst-surface promoter in a proportion of at least about 0.05% by weight of the catalyst.

175. The process as set forth in claim 174 wherein the catalyst-surface promoter comprises bismuth, tin, cadmium, magnesium, manganese, nickel, aluminum, cobalt, lead, titanium, antimony, selenium, iron, rhenium, zinc, cerium, zirconium, tellurium, or germanium.

176. The process as set forth in claim 174 further comprising introducing a supplemental promoter into the reactor system and mixing it with the particulate catalyst.

177. The process as set forth in claim 176 wherein the supplemental promoter is introduced into the liquid reaction medium within at least one of the oxidation reaction zones.

178. The process as set forth in claim 177 wherein the supplemental promoter is introduced into the first oxidation reaction zone.

179. The process as set forth in claim 176 wherein the supplemental promoter is introduced into the reactor system continuously or intermittently.

180. The process as set forth in claim 176 wherein the supplemental promoter introduced into the reactor system increases the activity and/or selectivity of the particulate catalyst for oxidizing formaldehyde or formic acid generated during the oxidation of the N-(phosphonomethyl)iminodiacetic acid substrate.

181. The process as set forth in claim 176 wherein the supplemental promoter introduced into the reactor system increases the activity and/or selectivity of the catalyst for oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate to form the N-(phosphonomethyl)glycine product.

182. The process as set forth in claim 176 wherein the supplemental promoter reduces noble metal leaching from the carbon support.

183. The process as set forth in claim 176 wherein the supplemental promoter comprises bismuth, lead, germanium, tellurium, titanium, copper and/or nickel.

184. The process as set forth in claim 183 wherein the supplemental promoter comprises bismuth.

185. The process as set forth in claim 184 wherein the supplemental promoter introduced into the reactor system is in the form of bismuth oxide, bismuth hydroxide, bismuth chloride, bismuth bromide, bismuth iodide, bismuth sulphide, bismuth selenide, bismuth telluride, bismuth sulphite, bismuth sulphate, bismuthyl sulfate, 5 bismuthyl nitrite, bismuth nitrate, bismuthyl nitrate, double nitrate of bismuth and magnesium, bismuth phosphite, bismuth phosphate, bismuth pyrophosphate, bismuthyl carbonate, bismuth perchlorate, bismuth antimonate, bismuth arsenate, bismuth selenite, bismuth titanate, bismuth vanadate, bismuth niobate, bismuth tantalate, bismuth chromate, bismuthyl dichromate, bismuthyl chromate, double 10 chromate of bismuthyl and potassium, bismuth molybdate, double molybdate of bismuth and sodium, bismuth tungstate, bismuth permanganate, bismuth zirconate, bismuth acetate, bismuthyl propionate, bismuth benzoate, bismuthyl salicylate, bismuth oxalate, bismuth tartrate, bismuth lactate, bismuth citrate, bismuth gallate, bismuth pyrogallate, bismuth phosphide, bismuth arsenide, sodium bismuthate, 15 bismuth-thiocyanic acid, sodium salt of bismuth-thiocyanic acid, potassium salt bismuth-thiocyanic acid, trimethylbismuthine, triphenylbismuthine, bismuth oxychloride, or bismuth oxyiodide.

186. The process as set forth in claim 185 wherein the supplemental promoter introduced into the reactor system is in the form of bismuth oxide.

187. The process as set forth in claim 186 wherein the supplemental promoter introduced into the reactor system is Bi_2O_3 .

188. A process for removal of water from an aqueous starting solution comprising N-(phosphonomethyl)glycine product and crystallization N-(phosphonomethyl)glycine product therefrom, the process comprising:
introducing an aqueous evaporation feed mixture into an evaporation zone,
5 said feed mixture comprising said aqueous starting solution;
evaporating water from said feed mixture in said evaporation zone in the presence of solid particulate N-(phosphonomethyl)glycine product, thereby producing a vapor phase comprising water vapor, precipitating N-(phosphonomethyl)glycine product from the aqueous liquid phase, and producing an evaporation product
10 comprising N-(phosphonomethyl)glycine product solids and a mother liquor that is substantially saturated or supersaturated in N-(phosphonomethyl)glycine product; and maintaining a ratio of particulate N-(phosphonomethyl)glycine product solids to mother liquor in said evaporation zone which exceeds the ratio of N-(phosphonomethyl)glycine product solids incrementally produced by the effects of
15 evaporation to mother liquor incrementally produced thereby.

189. The process as set forth in claim 188 wherein said evaporation product is divided to provide an N-(phosphonomethyl)glycine product solids fraction that is relatively depleted in mother liquor and a mother liquor fraction that is relatively depleted in N-(phosphonomethyl)glycine product solids.

190. The process as set forth in claim 189 wherein maintaining said ratio of particulate N-(phosphonomethyl)glycine product solids to mother liquor in said evaporation zone comprises returning solids obtained in said solids fraction to said evaporation zone or retaining solids obtained in said solid fraction within said zone.

191. The process as set forth in claim 190 comprising:
introducing an evaporation feed mixture comprising said aqueous starting solution into a vapor/liquid separation zone of said evaporation zone wherein the

pressure is below the vapor pressure of said mixture, thereby allowing water to flash
5 from the evaporation feed mixture, producing a vapor phase comprising water vapor, and precipitating N-(phosphonomethyl)glycine product from the liquid phase to produce a first slurry stream comprising particulate N-(phosphonomethyl)glycine product in a saturated or supersaturated mother liquor;
separating said vapor phase from said first slurry stream;
10 introducing said first slurry stream into a retention zone in which a supernatant liquid comprising a fraction of said mother liquor is separated from a second slurry stream comprising precipitated N-(phosphonomethyl)glycine product and mother liquor, said retention zone having an inlet for said first slurry, a decantation liquid exit for said supernatant liquid spaced above said inlet, and an exit for said second slurry spaced above said inlet but below said decantation liquid exit; and
15 maintaining the relative rates at which said first slurry is introduced into said retention zone, said second slurry is drawn off through said second slurry exit and said supernatant liquid is drawn off through said decantation liquid exit such that the upward flow velocity in a lower region of said retention zone below said second slurry exit is sufficient to maintain precipitated N-(phosphonomethyl)glycine product in suspension in the liquid phase while the upward flow velocity in an upper region of said retention zone above said second slurry exit is below the sedimentation velocity of at least 80% by weight of the N-(phosphonomethyl)glycine product particles in said lower region.

192. The process as set forth in claim 191 wherein at least a portion of said second slurry stream is recirculated to said vapor/liquid separation zone.

193. The process as set forth in claim 192 wherein at least a portion of said second slurry stream and said aqueous starting solution together comprise the evaporation feed mixture introduced into said vapor/liquid separation zone.

194. The process as set forth in claim 193 wherein said aqueous starting solution and said second slurry stream are mixed before introduction into said vapor/liquid separation zone.

195. The process as set forth in claim 193 wherein a third slurry stream is removed from said lower region of said zone.

196. The process as set forth in claim 195 wherein said third slurry stream is removed from said lower region through a slurry exit separate from said second slurry exit.

197. The process as set forth in claim 195 wherein said third slurry stream is obtained by dividing said second slurry stream into a recirculation stream and said third slurry stream.

198. The process as set forth in claim 195 wherein the relative rates of the flow of said aqueous starting solution to said vapor/liquid separation zone, recirculation of all or part of said second slurry stream to said vapor/liquid separation zone, withdrawal of said supernatant liquid from said decantation liquid exit,
5 withdrawal of said third slurry stream from said lower region of said retention zone, and return to said evaporation zone of any liquid or solids bearing streams from any solids/liquid separations to which said third slurry may be subjected, are sufficient to establish a ratio of N-(phosphonomethyl)glycine product solids to mother liquor in said lower region of said zone that is higher than the ratio of precipitated solid N-
10 (phosphonomethyl)glycine product incrementally produced by the effects of evaporation to mother liquor incrementally produced thereby.

199. The process as set forth in claim 198 wherein the relative flow rates of said streams are controlled so that the N-(phosphonomethyl)glycine product solids

concentration in said lower region of said zone is at least about twice the concentration of N-(phosphonomethyl)glycine product solids in the mixture of such 5 solids and mother liquor that is or would be produced by flashing of said aqueous starting solution in said vapor/liquid zone in the absence of said recirculated second slurry stream.

200. The process as set forth in claim 199 wherein solids are removed from said third slurry to produce a recycle liquid fraction which is recirculated to said vapor/liquid separation zone, whereby said evaporation feed mixture further comprises said recycle liquid fraction.

201. The process as set forth in claim 200 wherein both said aqueous starting solution and said recycle liquid fraction are mixed with said second slurry stream prior to introduction into said vapor/liquid separation zone.

202. The process as set forth in claim 201 wherein the relative flow rates of all of said streams, including said recycle liquid fraction, are controlled so that the solids content of the slurry in said lower region of said zone is at least about 12% by weight.

203. The process as set forth in claim 201 wherein the relative flow rates of said streams are controlled so that solids removed from said third slurry have a median cube weighted particle size of at least about 200 μm .

204. The process as set forth in claim 201 wherein the relative flow rates of said streams are controlled so that the solids removed from said third slurry have a BET surface area not greater than about 0.09 m^2/g .

205. The process as set forth in claim 203 wherein the upward flow velocity in said lower region is at least four times the sedimentation velocity of at least 80% by weight of the solids contained therein, and the upward flow velocity in the upper region of the zone is less than one fourth the sedimentation velocity of at least 80%
5 by weight of the solids in said second slurry.

206. The process as set forth in claim 199 wherein said feed mixture comprises a slurry of N-(phosphonomethyl)glycine product in an aqueous liquid phase that is supersaturated in N-(phosphonomethyl)glycine product, said feed mixture flowing along a recirculation path between said second slurry exit and an inlet
5 to said vapor/liquid separation zone without substantial axial back-mixing.

207. The process as set forth in claim 206 wherein the surface area of the solids contained in said feed mixture is sufficient to allow production of crystalline N-(phosphonomethyl)glycine product having a median cube weighted particle size of at least about 200 μm .

208. The process as set forth in claim 207 wherein the maximum extent of supersaturation expressed as the difference between the N-(phosphonomethyl)glycine product concentration in the aqueous liquid phase at any location within said recirculation path and the saturation concentration of N-(phosphonomethyl)glycine
5 product in the aqueous liquid phase at such location is not greater than about 0.7% by weight, basis the aqueous liquid phase.

209. The process as set forth in claim 207 wherein the integrated average extent of supersaturation expressed as the difference between the N-(phosphonomethyl)glycine product concentration in the aqueous liquid phase and the saturation concentration of N-(phosphonomethyl)glycine product in the aqueous

5 liquid phase over said recirculation path is not greater than about 0.5% by weight,
basis the aqueous liquid phase.

210. The process as set forth in claim 207 wherein the integrated average extent of supersaturation expressed as the difference between the N-(phosphonomethyl)glycine product concentration in the aqueous liquid phase and the saturation concentration of N-(phosphonomethyl)glycine product in the aqueous 5 liquid phase over said recirculation path is at least 0.2% lower than the extent of supersaturation required to provide the same crystallization productivity per unit working volume of a reference evaporator consisting of a fully back mixed evaporation zone in which the ratio of N-(phosphonomethyl)glycine product solids to mother liquor is equal to the ratio of N-(phosphonomethyl)glycine product solids 10 incrementally produced by the effects of the evaporation to mother liquor incrementally produced thereby.

211. The process as set forth in claim 199 wherein the rate of recirculation of said second slurry to said vapor/liquid separation zone is at least about 20 times the rate of withdrawal of said supernatant liquid from said decantation liquid exit.

212. The process as set forth in claim 191 wherein said vapor/liquid separation zone is positioned above the interface between said lower region and said upper region of said retention zone and is segregated from said upper region, said vapor/liquid separation zone being in fluid flow communication with the lower region 5 of said retention zone via a draft tube for flow of said first slurry from said separation zone to said lower region.

213. The process as set forth in claim 191 which is operated substantially without transfer of heat to or from said vapor/liquid separation zone, said retention zone, said feed mixture or said second slurry.

214. The process as set forth in claim 191 wherein precipitation of N-(phosphonomethyl)glycine product upon evaporation results primarily from cooling of the aqueous liquid phase in the evaporation zone.

215. The process as set forth in claim 191 comprising:
- removing an evaporation product slurry from said lower region of said retention zone;
- subjecting said evaporation product slurry to solids/liquid separation to
- 5 provide an N-(phosphonomethyl)glycine product solids fraction that is relatively depleted in mother liquor and a mother liquor fraction that is relatively depleted in N-(phosphonomethyl)glycine product solids; and
- returning solids obtained in said solids fraction to said evaporation zone or
- retaining solids obtained in said solid fraction within said zone, thereby maintaining a
- 10 ratio of particulate N-(phosphonomethyl)glycine product solids to mother liquor in
- said evaporation zone which exceeds the ratio of N-(phosphonomethyl)glycine
- product solids produced by the evaporation to mother liquor produced thereby.

216. A method for removal of water from an aqueous starting solution comprising N-(phosphonomethyl)glycine product and crystallization of N-(phosphonomethyl)glycine product therefrom, the process comprising:
- introducing an evaporation feed mixture comprising said aqueous starting
- 5 solution into a vapor/liquid separation zone wherein the pressure is below the vapor pressure of said mixture, thereby allowing water to flash from the evaporation feed mixture, producing a vapor phase comprising water vapor and increasing the concentration of N-(phosphonomethyl)glycine product in the remaining liquid phase to a concentration in excess of the solubility of N-(phosphonomethyl)glycine product,
- 10 whereby N-(phosphonomethyl)glycine product precipitates from the liquid phase to produce a first slurry stream comprising particulate N-(phosphonomethyl)glycine product in a saturated or supersaturated mother liquor;

separating said vapor phase from said first slurry stream;
introducing said first slurry stream into a decantation zone in which a
15 supernatant liquid comprising a fraction of said mother liquor is separated from a
second slurry stream comprising precipitated N-(phosphonomethyl)glycine product
and mother liquor, said decantation zone having an inlet for said first slurry, a
decantation liquid exit for said supernatant liquid spaced above said inlet, and an exit
for said second slurry vertically spaced above said inlet but below said supernatant
20 liquid exit; and
maintaining the relative rates at which said first slurry is introduced into said
decantation zone, said second slurry is drawn off through said second slurry exit and
said supernatant liquid is drawn off through said decantation liquid exit such that the
upward flow velocity in a lower region of said decantation zone below said second
25 slurry exit is sufficient to maintain precipitated N-(phosphonomethyl)glycine product
in suspension in the liquid phase while the upward flow velocity in an upper region of
said decantation zone above said second slurry exit is below the sedimentation
velocity of at least 80% by weight of the N-(phosphonomethyl)glycine product
particles in said lower region.

217. A process for removal of water from an aqueous starting solution
comprising N-(phosphonomethyl)glycine product and crystallization N-
(phosphonomethyl)glycine product therefrom, the process comprising:

introducing an aqueous evaporation feed mixture into an evaporation zone,
5 said feed mixture comprising said aqueous starting solution;
evaporating water from said feed mixture in said evaporation zone in the
presence of solid particulate N-(phosphonomethyl)glycine product, thereby producing
a vapor phase comprising water vapor, precipitating N-(phosphonomethyl)glycine
product from the aqueous liquid phase, and producing an evaporation product
10 comprising N-(phosphonomethyl)glycine product solids and a mother liquor that is
substantially saturated or supersaturated in N-(phosphonomethyl)glycine product;

dividing said evaporation product to provide an N-(phosphonomethyl)glycine product solids fraction that is relatively depleted in mother liquor and a mother liquor fraction that is relatively depleted in N-(phosphonomethyl)glycine product solids; and

15 maintaining a ratio of particulate N-(phosphonomethyl)glycine product solids to mother liquor in said evaporation zone that exceeds the ratio of N-(phosphonomethyl)glycine product solids incrementally produced by the effects of evaporation to mother liquor incrementally produced thereby.

218. A process for the preparation of an N-(phosphonomethyl)glycine product comprising:
- introducing an aqueous feed mixture comprising an N-(phosphonomethyl)iminodiacetic acid substrate into a liquid reaction medium;
- 5 catalytically oxidizing N-(phosphonomethyl)iminodiacetic acid substrate in said aqueous liquid reaction medium thereby producing a reaction mixture comprising N-(phosphonomethyl)glycine product;
- cooling a primary crystallization feed mixture comprising N-(phosphonomethyl)glycine product produced in said reaction mixture, thereby
- 10 precipitating N-(phosphonomethyl)glycine product and producing a primary mother liquor comprising N-(phosphonomethyl)glycine product;
- separating precipitated N-(phosphonomethyl)glycine product from said primary mother liquor; and
- recycling primary mother liquor and introducing it into said liquid reaction
- 15 medium wherein N-(phosphonomethyl)iminodiacetic acid substrate is oxidized to N-(phosphonomethyl)glycine product.

219. The process as set forth in claim 218 wherein said reaction mixture is divided into a primary fraction and a secondary fraction, said primary crystallization feed mixture comprising N-(phosphonomethyl)glycine product obtained in said primary fraction.

220. The process as set forth in claim 219 wherein N-(phosphonomethyl)glycine product is crystallized from a secondary crystallizer feed mixture comprising N-(phosphonomethyl)glycine product obtained in said secondary fraction, thereby producing a secondary mother liquor comprising N-(phosphonomethyl)glycine product and by-products of said oxidation reaction.

221. The process as set forth in claim 220 wherein an aqueous secondary reactor feed mixture, comprising N-(phosphonomethyl)glycine product obtained in said secondary fraction and unreacted N-(phosphonomethyl)iminodiacetic acid substrate contained therein, is introduced into a secondary oxidation zone wherein unreacted N-(phosphonomethyl)iminodiacetic acid substrate is oxidized to produce a secondary oxidation reaction mixture containing additional N-(phosphonomethyl)glycine product, said secondary crystallizer feed mixture comprising said secondary oxidation reaction mixture.

222. The process as set forth in claim 221 wherein said secondary oxidation zone comprises a fixed bed containing a catalyst for the oxidation.

223. The process as set forth in claim 220 wherein crystallization of N-(phosphonomethyl)glycine product from said primary crystallization feed mixture comprises evaporative cooling of said primary feed mixture.

224. The process as set forth in claim 223 wherein water constituting between about 5% and about 30% by weight of said primary crystallization feed mixture is removed in evaporative cooling thereof.

225. The process as set forth in claim 223 wherein said evaporative cooling is conducted substantially adiabatically.

226. The process as set forth in claim 224 wherein crystallization of said N-(phosphonomethyl)glycine product from said secondary crystallization feed mixture comprises heat-driven evaporative crystallization.

227. The process as set forth in claim 218 wherein N-(phosphonomethyl)iminodiacetic acid substrate is oxidized in said aqueous liquid reaction medium in a primary oxidation reaction zone, thereby producing a primary oxidation product, the process further comprising:

5 dividing said primary oxidation product into a finishing reaction feed mixture and a primary crystallization fraction, said aqueous crystallization feed mixture comprising said primary crystallization fraction;

introducing said finishing reaction feed mixture into a finishing reaction zone;
and

10 catalytically oxidizing residual N-(phosphonomethyl)iminodiacetic acid substrate contained in said finishing reaction feed mixture to N-(phosphonomethyl)glycine product to produce a finished reaction mixture.

228. The process as set forth in claim 227 wherein said primary oxidation product contains between about 0.5% and about 2% by weight unreacted N-(phosphonomethyl)iminodiacetic acid.

229. The process as set forth in claim 228 wherein a secondary crystallizer feed mixture comprising N-(phosphonomethyl)glycine product obtained in said finished reaction mixture is subjected to heat-driven evaporative crystallization, thereby precipitating N-(phosphonomethyl)glycine product and producing a

5 secondary mother liquor comprising N-(phosphonomethyl)glycine product and by-products of the oxidation of N-(phosphonomethyl)iminodiacetic acid substrate.

230. The process as set forth in claim 218 wherein N-(phosphonomethyl)iminodiacetic acid substrate is continuously oxidized in the presence of a noble metal on carbon catalyst.

231. A process for the preparation of an N-(phosphonomethyl)glycine product comprising:

- introducing an aqueous feed mixture comprising an N-(phosphonomethyl)iminodiacetic acid substrate into a catalytic reactor system
- 5 comprising one or more catalytic reaction zones;
- catalytically oxidizing N-(phosphonomethyl)iminodiacetic acid substrate to N-(phosphonomethyl)glycine product in said catalytic reactor system to produce a product mixture;
- 10 dividing said product mixture into a primary fraction and a secondary fraction;
- crystallizing N-(phosphonomethyl)glycine product from said primary fraction to produce a solid N-(phosphonomethyl)glycine product fraction and a primary mother liquor;
- recycling primary mother liquor for use as a source of water in the preparation of said feed mixture.

232. The process as set forth in claim 231 wherein substantially all of said primary mother liquor is recycled as a source of water in the preparation of said feed mixture.

233. The process as set forth in claim 231 wherein N-(phosphonomethyl)glycine is crystallized from said primary fraction by evaporative crystallization.

234. The process as set forth in claim 233 wherein additional N-(phosphonomethyl)glycine is crystallized from said secondary fraction, thereby producing a secondary mother liquor.

235. The process as set forth in claim 234 wherein N-(phosphonomethyl)glycine is crystallized from said secondary fraction by evaporative crystallization.

236. The process as set forth in claim 235 wherein N-(phosphonomethyl)glycine is crystallized from said primary fraction by substantially adiabatic evaporative crystallization.

237. The process as set forth in claim 235 wherein said feed mixture is continuously introduced into said reactor system, a reaction zone within said system being substantially back-mixed with respect to the liquid phase therein, the exothermic heat of reaction serving to heat the contents of the feed mixture to the reaction temperature prevailing in said back-mixed reaction zone.

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238. The process as set forth in claim 237 wherein the catalyst for said reaction comprises a noble metal and is effective to oxidize C₁ by-products selected from the group consisting of formaldehyde and formic acid, the oxidation of said C₁ by-products further contributing to heating the contents of said aqueous feed mixture.

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239. The process as set forth in claim 231 wherein N-(phosphonomethyl)iminodiacetic acid is oxidized in the presence of heterogeneous catalyst comprising a noble metal, a fraction of noble metal is leached from said catalyst in said catalytic oxidation reactor system, leached noble metal contained in said primary fraction being returned to said catalytic reactor system in said primary mother liquor.

240. The process as set forth in claim 239 wherein leached noble metal contained in said recycle primary mother liquor inhibits further leaching of noble metal from said catalyst in said catalytic reactor system.

241. The process as set forth in claim 239 wherein a portion of leached noble metal contained in said recycle mother liquor is redeposited on the surface of said heterogeneous catalyst in said catalytic reactor system.

242. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:

- 5 introducing a liquid phase feed stream comprising an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into a primary oxidation reaction zone, the primary oxidation reaction zone comprising a primary fixed bed containing an oxidation catalyst;
- 10 introducing an oxidizing agent into the primary oxidation reaction zone; continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate to the N-(phosphonomethyl)glycine product in the primary oxidation reaction zone, thereby producing a primary reaction mixture comprising the N-(phosphonomethyl)glycine product and unreacted N-(phosphonomethyl)iminodiacetic acid substrate;
- 15 withdrawing the primary reaction mixture from the primary oxidation reaction zone; and maintaining the difference in unit weight sensible heat content between said reaction mixture and said aqueous feed stream less than the exothermic reaction heat generated in the reaction zone per unit weight of the aqueous feed stream.

243. The process as set forth in claim 242 wherein maintaining the difference in unit weight sensible heat content between said reaction mixture and said aqueous feed stream less than the exothermic reaction heat generated in the reaction zone per unit weight of the aqueous feed stream comprises cooling of said fixed bed by indirect transfer of heat to a heat transfer or process fluid flowing through a conduit within or in contact with said bed.

244. The process as set forth in claim 242 wherein maintaining the difference in unit weight sensible heat content between said reaction mixture and said aqueous feed stream less than the exothermic reaction heat generated in the reaction zone per unit weight of the aqueous feed stream comprises introducing into said bed a recirculation fraction comprising N-(phosphonomethyl)glycine product produced in the reaction wherein said recirculation fraction has been cooled externally of said fixed bed.

245. The process as set forth in claim 244 comprising:
dividing the primary reaction mixture into a primary product fraction and a primary reactor circulation fraction;
passing the primary reaction mixture or the primary reactor recirculation fraction through a heat exchanger for removal of heat of oxidation of the N-(phosphonomethyl)iminodiacetic acid substrate; and
returning the primary reactor recirculation fraction to the primary oxidation reaction zone.

246. The process as set forth in claim 245 wherein said primary reaction mixture is passed through said heat exchanger before said primary reaction mixture is divided.

247. The process as set forth in claim 245 wherein the ratio of the volumetric flow rate of the primary reactor recirculation fraction to the volumetric flow rate of the primary product fraction is at least about 0.5:1.

248. The process as set forth in claim 247 wherein the ratio of the volumetric flow rate of the primary reactor recirculation fraction to the volumetric flow rate of the primary product fraction is from about 1:1 to about 10:1.

249. The process as set forth in claim 244 wherein the aqueous feed stream and the primary reactor recirculation fraction are mixed to produce a combined inlet stream, the liquid phase feed stream introduced into the oxidation reaction zone comprising said combined inlet feed stream.

250. The process as set forth in claim 249 wherein the aqueous feed stream comprises a slurry of N-(phosphonomethyl)iminodiacetic acid substrate in a substantially saturated aqueous solution of N-(phosphonomethyl)iminodiacetic acid substrate, and the primary reactor recirculation fraction has a lower N-

5 (phosphonomethyl)iminodiacetic acid substrate content than the aqueous feed stream, whereby the combined inlet stream obtained by mixing the aqueous feed stream with the primary reactor recirculation fraction is substantially free of N-(phosphonomethyl)iminodiacetic acid substrate solids under the conditions prevailing at the liquid inlet region of the primary fixed bed.

251. The process as set forth in claim 250 wherein the aqueous feed stream comprises a slurry containing between about 8% and about 15% N-(phosphonomethyl)iminodiacetic acid substrate and the primary reactor recirculation fraction comprises a solution containing between about 0.5% and about 5% by weight 5 N-(phosphonomethyl)iminodiacetic acid substrate.

252. The process as set forth in claim 242 further comprising:
introducing a second reactor feed mixture comprising at least a portion of the primary product fraction into a second oxidation reaction zone, the second oxidation reaction zone comprising a second fixed bed containing an oxidation catalyst;
5 introducing an oxidizing agent into the second oxidation reaction zone; and continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate and a by-product C₁ compound in the second oxidation reaction zone to produce a second reaction product mixture containing N-(phosphonomethyl)glycine product.

253. The process as set forth in claim 252 wherein at least 95% of the N-(phosphonomethyl)iminodiacetic acid substrate contained in the aqueous feed stream is oxidized in the primary and second oxidation reaction zones.

254. The process as set forth in claim 253 wherein at least 98% of the N-(phosphonomethyl)iminodiacetic acid substrate contained in the aqueous feed stream is oxidized in the primary and second oxidation reaction zones.

255. The process as set forth in claim 242 wherein the primary fixed bed in the primary oxidation reaction zone contains a noble metal on carbon catalyst.

256. The process as set forth in claim 255 wherein the primary fixed bed in the primary oxidation reaction zone contains a carbon catalyst without a noble metal.

257. The process as set forth in claim 256 further comprising:
introducing at least a portion of the second reaction mixture into a third oxidation reaction zone comprising a fixed bed containing an oxidation catalyst;
introducing an oxidizing agent into the third oxidation reaction zone; and

5 continuously oxidizing a by-product C₁ compound in the third oxidation reaction zone to produce a third reaction product mixture containing N-(phosphonomethyl)glycine product.

258. The process as set forth in claim 257 further comprising oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate in the third oxidation reaction zone.

259. The process as set forth in claim 257 wherein the fixed bed in the third oxidation reaction zone contains a noble metal on carbon catalyst, reaction in the third oxidation reaction zone comprising catalytic oxidation of C₁ compound remaining in the second reaction mixture.

260. The process as set forth in claim 257 wherein the liquid phase reacting mixture passes through the third fixed bed in substantially plug flow and substantially without recirculation of said third reaction product mixture or other effluent therefrom.

261. The process as set forth in claim 260 wherein the third oxidation reaction zone is operated substantially without back-mixing of the liquid phase reacting mixture.

262. The process as set forth in claim 255 wherein the fixed bed in the primary oxidation reaction zone contains a noble metal on carbon catalyst, a C₁ compound being oxidized in the primary oxidation reaction zone.

263. The process as set forth in claim 252 wherein the liquid phase reacting mixture passes through the second fixed bed in substantially plug flow and substantially without recirculation of said second reaction product mixture or other effluent therefrom .

264. The process as set forth in claim 252 wherein the second oxidation reaction zone is operated substantially without back-mixing of the liquid phase reacting mixture.

265. The process as set forth in claim 252 further comprising transferring heat of reaction generated in the second oxidation reaction zone to a cooling fluid.

266. The process as set forth in claim 252 wherein the second oxidation reaction zone operates substantially adiabatically.

267. The process as set forth in claim 242 wherein the oxidizing agent is an O₂-containing gas and the integrated average oxygen partial pressure over the liquid phase flow path in the primary oxidation reaction zone is at least about 50 psia.

268. The process as set forth in claim 267 wherein the integrated average oxygen partial pressure over the liquid phase flow path in the primary oxidation reaction zone is at least about 100 psia.

269. The process as set forth in claim 267 wherein the oxygen concentration of the gas phase at the gas exit of the reactor is between about 20% and about 30% by volume.

270. The process as set forth in claim 267 wherein oxygen utilization in the primary oxidation reaction zone is between about 50% and about 95%.

271. The process as set forth in claim 242 wherein the integrated average temperature of the liquid phase across the liquid phase flow path through the primary oxidation reaction zone is between about 80°C and about 130°C.

272. The process as set forth in claim 242 wherein the integrated average temperature of the liquid phase across the liquid phase flow path through the primary oxidation reaction zone is between about 105°C and about 120°C.

273. The process as set forth in claim 242 wherein the ratio of catalyst surface area to volume of liquid phase reacting mixture in the primary fixed bed is from about 100 to about 6000 m²/cm³.

274. The process as set forth in claim 273 wherein the ratio of catalyst surface area to volume of liquid phase reacting mixture in the primary fixed bed is from about 200 to about 2000 m²/cm³.

275. The process as set forth in claim 242 wherein the oxidizing agent is an O₂-containing gas and the liquid phase and the gas phase flow co-currently through the primary fixed bed.

276. The process as set forth in claim 242 wherein the oxidizing agent is an O₂-containing gas and the liquid phase and the gas phase flow countercurrently through the primary fixed bed.

277. The process as set forth in claim 242 wherein the catalyst activity within the primary fixed bed varies along the liquid phase flow path through the reactor, the activity of the catalyst in an upstream section of the primary fixed bed with respect to the direction of liquid phase flow being lower than the catalyst activity in a downstream section.

278. A process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:

introducing an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into the first of a series of oxidation reaction zones, each of the series of oxidation reaction zones comprising an oxidation catalyst;

5 oxidizing the an N-(phosphonomethyl)iminodiacetic acid substrate in the first oxidation reaction zones to produce an intermediate oxidation reaction product;

10 introducing the intermediate oxidation reaction product into a second oxidation reaction zone comprising a fixed bed containing a noble metal on carbon catalyst; and

oxidizing by-product formaldehyde and/or formic acid in the second oxidation reaction zone.

279. The process as set forth in claim 278 wherein the first and second oxidation reaction zones comprise continuous oxidation reaction zones, the aqueous feed stream being continuously or intermittently introduced into the first oxidation reaction zone, the intermediate oxidation product being continuously or intermittently withdrawn from the first oxidation reaction zone and continuously or intermittently introduced into the second oxidation reaction zone.

280. The process as set forth in claim 279 wherein the intermediate oxidation reaction product is cooled prior to being introduced into the second oxidation reaction zone.

281. The process as set forth in claim 280 wherein each of the oxidation reaction zones comprises a fixed bed containing a catalyst for the oxidation of N-(phosphonomethyl)iminodiacetic acid substrate to N-(phosphonomethyl)glycine product, each except the last of the series producing an intermediate reaction product which is introduced into the next succeeding oxidation reaction zone in the series, and

a final reaction product comprising N-(phosphonomethyl)glycine product being withdrawn from the last of the oxidation reaction zones.

282. The process as set forth in claim 281 wherein the series comprises more than two oxidation reaction zones, the intermediate reaction mixture exiting each of the first two of the oxidation reaction zones being cooled before being introduced into the next succeeding oxidation reaction zone.

283. The process as set forth in claim 282 wherein the intermediate reaction mixture is cooled before being introduced into the next succeeding oxidation reaction zone.

284. The process as set forth in claim 282 wherein said aqueous feed mixture contains at least about 15% by weight of a water-soluble salt of N-(phosphonomethyl)iminodiacetic acid on an acid equivalent basis and said final reaction mixture contains at least about 12% by weight of a water-soluble salt of N-
5 (phosphonomethyl)glycine on an acid equivalent basis.

285. The process as set forth in claim 284 wherein said aqueous feed mixture contains at least about 25% by weight of a water-soluble salt of N-(phosphonomethyl)iminodiacetic acid on an acid equivalent basis and said final oxidation reaction mixture contains at least about 20% by weight of a water-soluble
5 salt of N-(phosphonomethyl)glycine on an acid equivalent basis.

286. The process as set forth in claim 285 wherein said aqueous feed mixture contains at least about 35% by weight of a water-soluble salt of N-(phosphonomethyl)iminodiacetic acid on an acid equivalent basis and said final oxidation reaction mixture contains at least about 28% by weight of a water-soluble
5 salt of N-(phosphonomethyl)glycine on an acid equivalent basis.

287. The process as set forth in claim 284 wherein a final oxidation reaction is concentrated by removal of water therefrom.

288. A process as set forth in claim 287 wherein said final reaction mixture is introduced into a flash evaporation zone wherein the pressure is lower than the vapor pressure of said final oxidation mixture at the temperature at which it exits the last of said series of reactors.

289. The process as set forth in claim 278 wherein the first oxidation reaction zone comprises a substantially back-mixed oxidation reaction zone within a continuous stirred tank reactor.

290. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:

- introducing an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reaction zone comprising a fixed bed containing an oxidation catalyst;
- 5 introducing an O₂-containing gas into the oxidation reaction zone; and continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate to the N-(phosphonomethyl)glycine product in the oxidation reaction zone, thereby
- 10 producing an oxidation reaction mixture comprising the N-(phosphonomethyl)glycine product, the ratio of the mass flow rate of the liquid phase to the mass flow rate of gas phase in the fixed bed being between about 20 and about 800.

291. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:
- introducing an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reaction zone
- comprising a fixed bed containing an oxidation catalyst;
- introducing an O₂-containing gas into the oxidation reaction zone; and
- continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate to N-(phosphonomethyl)glycine product in the oxidation reaction zone, thereby
- producing an oxidation reaction mixture comprising the N-(phosphonomethyl)glycine product, the volumetric ratio of the liquid phase holdup in the fixed bed to the total bed volume being between about 0.1 and about 0.5.
292. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:
- introducing an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reaction zone
- comprising a fixed bed containing an oxidation catalyst;
- introducing an O₂-containing gas into the oxidation reaction zone; and
- continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate to the N-(phosphonomethyl)glycine product in the oxidation reaction zone, thereby
- producing an oxidation reaction mixture comprising the N-(phosphonomethyl)glycine product, the partial pressure of oxygen at the liquid exit of the fixed bed being not greater than about 100 psia.
293. The process as set forth in claim 292 wherein the partial pressure of oxygen at the liquid exit of the fixed bed is between about 10 and about 50 psia.

294. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:
- introducing an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reaction zone
- comprising a fixed bed containing an oxidation catalyst;
- introducing an O₂-containing gas into the oxidation reaction zone; and
- continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate to the N-(phosphonomethyl)glycine product in the oxidation reaction zone, thereby
- producing an oxidation reaction mixture comprising the N-(phosphonomethyl)glycine product, the partial pressure of oxygen being not greater than about 50 psia at any location in the fixed bed at which the concentration of N-(phosphonomethyl)iminodiacetic acid substrate in the liquid phase is lower than about 0.1 ppm.
295. The process as set forth in claim 294 wherein the partial pressure of oxygen is not greater than about 50 psia at any location in the fixed bed at which the concentration of N-(phosphonomethyl)iminodiacetic acid substrate in the liquid phase is lower than about 0.2 ppm.
296. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:
- introducing an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reaction zone
- comprising a fixed bed containing an oxidation catalyst, the catalyst surface area to liquid holdup in the fixed bed being between about 100 and about 6000 m²/cm³;
- introducing an oxidizing agent into the oxidation reaction zone; and

continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate
10 to the N-(phosphonomethyl)glycine product in the oxidation reaction zone, thereby
producing an oxidation reaction mixture comprising the N-(phosphonomethyl)glycine
product.

297. The process as set forth in claim 296 wherein the ratio of catalyst surface area to liquid holdup in the fixed bed is between about 200 and about 2000 m²/cm³.

298. The process as set forth in claim 297 wherein the ratio of catalyst surface area to liquid holdup in the fixed bed is between about 400 and about 1500 m²/cm³.

299. The process as set forth in claim 297 wherein the catalyst comprises platinum on carbon and the platinum loading on the catalyst is less than 70% of the loading required to provide equivalent productivity in lbs. N-(phosphonomethyl)glycine product per hour per pound of catalyst at the same
5 temperature in continuous stirred tank reactor utilizing a platinum on carbon a slurry catalyst.

300. The process as set forth in claim 297 wherein the catalyst comprises a platinum on carbon catalyst containing less than 3 wt% platinum.

301. The process as set forth in claim 296 wherein the integrated average partial pressure of oxygen along the liquid flow path in the fixed bed is at least about 50 psia.

302. The process as set forth in claim 296 wherein the integrated average temperature of the liquid phase in the fixed bed is between about 80°C and about 130°C.

303. The process as set forth in claim 296 wherein the partial pressure of oxygen is not greater than about 50 psia at any location in the fixed bed at which the concentration of N-(phosphonomethyl)iminodiacetic acid substrate in the liquid phase is lower than about 0.1 ppm.

304. The process as set forth in claim 297 wherein the partial pressure of oxygen is not greater than about 50 psia at any location in the fixed bed at which the concentration of N-(phosphonomethyl)iminodiacetic acid substrate in the liquid phase is lower than about 0.2 ppm.

305. A process as set forth in claim 296 wherein the oxygen utilization in the oxidation reaction zone is between about 50% and about 95%.

306. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:

- introducing an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reaction zone comprising a fixed bed containing an oxidation catalyst;
- 5 introducing an O₂-containing gas into the oxidation reaction zone; and continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate to the N-(phosphonomethyl)glycine product in the oxidation reaction zone, thereby
- 10 producing an oxidation reaction mixture comprising the N-(phosphonomethyl)glycine product, the integrated average partial pressure of oxygen along the liquid flow path in the fixed bed being at least about 50 psia and the integrated average temperature of the liquid phase in the fixed bed being between about 80°C and about 130°C.

307. The process as set forth in claim 306 wherein the integrated average partial pressure of oxygen along the liquid flow path in the fixed bed is at least about

100 psia and the integrated average temperature of the liquid phase in the fixed bed is between about 105°C and about 120°C.

308. The process as set forth in claim 306 wherein the oxygen partial pressure at the liquid exit of the fixed bed is not greater than about 100 psia.

309. The process as set forth in claim 306 wherein the oxygen partial pressure is not greater than about 50 psia at any location in the bed wherein the concentration of N-(phosphonomethyl)iminodiacetic acid substrate in the liquid phase is lower than about 0.1 ppm.

310. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:

- introducing an aqueous feed stream comprising the N-(phosphonomethyl)iminodiacetic acid substrate into an oxidation reaction zone comprising a fixed bed containing oxidation catalyst bodies and other means for promoting gas/liquid mass transfer;
- 5 introducing an O₂-containing gas into the oxidation reaction zone; and continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate to the N-(phosphonomethyl)glycine product in the oxidation reaction zone, thereby producing an oxidation reaction mixture comprising the N-(phosphonomethyl)glycine product.
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311. The process as set forth in claim 310 wherein said other means for promoting gas/liquid mass transfer comprises inert packing.

312. The process as set forth in claim 311 wherein said packing functions as a diluent for the catalyst, thereby modulating the activity of the catalyst bed.

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313. The process as set forth in claim 312 wherein the activity of the catalyst bed varies in the direction of fluid flow as a function of variation of the surface area of the catalyst bodies relative to the surface area of the inert packing in said direction.

314. The process as set forth in claim 311 wherein said inert packing is selected from the group consisting of rings, saddles and structured packing.

315. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, the process comprising:

introducing a liquid phase feed stream comprising an aqueous feed **mixture** 5 comprising the N-(phosphonomethyl)iminodiacetic acid substrate into a primary oxidation reaction zone, the primary oxidation reaction zone comprising a fixed bed containing an oxidation catalyst;

introducing an oxidizing agent into the primary oxidation reaction zone;
continuously oxidizing the N-(phosphonomethyl)iminodiacetic acid substrate 10 to the N-(phosphonomethyl)glycine product in the primary oxidation reaction zone, thereby producing a liquid phase exit stream comprising a primary reaction mixture comprising the N-(phosphonomethyl)glycine product and unreacted N-(phosphonomethyl)iminodiacetic acid substrate; and

15 withdrawing said liquid phase exit stream from the primary oxidation reaction zone; the rate of introduction of said liquid phase feed stream and withdrawal of said liquid phase exit stream being such that the liquid phase hourly space velocity in said fixed bed based on total bed volume is between about 0.5 hr^{-1} and about 20 hr^{-1} .

316. The process as set forth in claim 315 wherein the liquid phase hourly space velocity in said fixed bed is between about 3 hr^{-1} and about 20 hr^{-1} .

317. The process as set forth in claim 315 wherein the conversion of N-(phosphonomethyl)iminodiacetic acid substrate to N-(phosphonomethyl)glycine product within said fixed bed is at least about 50%.

318. The process as set forth in claim 315 wherein said liquid hourly space velocity is between about 0.5 hr⁻¹ and about 5 hr⁻¹ and the conversion of N-(phosphonomethyl)iminodiacetic acid substrate to N-(phosphonomethyl)glycine product within said fixed bed is at least about 95%.

319. The process as set forth in claim 315 wherein the residual N-(phosphonomethyl)iminodiacetic acid substrate in said primary oxidation reaction mixture is not greater than about 0.2 ppm.

320. A process as set forth in claim 319 wherein said aqueous feed mixture contains at least about 15% by weight of a water-soluble salt of N-(phosphonomethyl)iminodiacetic acid on an acid equivalent basis, and wherein a final reaction mixture is produced which contains at least about 12% by weight of a water-soluble salt of N-(phosphonomethyl)glycine on an acid equivalent basis, said final oxidation reaction mixture comprising said primary oxidation reaction mixture, a primary product comprising a fraction of said primary oxidation reaction mixture, or a further reaction mixture obtained by introducing said primary reaction mixture or said primary product fraction into a secondary reaction system comprising one or more additional reaction zones for further oxidation of N-(phosphonomethyl)iminodiacetic acid substrate to N-(phosphonomethyl)glycine product and/or oxidation of formaldehyde or formic acid.

321. The process as set forth in claim 320 wherein said aqueous feed mixture contains at least about 25% by weight of a water-soluble salt of N-(phosphonomethyl)iminodiacetic acid on an acid equivalent basis and said final

oxidation reaction mixture contains at least about 20% by weight of a water-soluble
5 salt of N-(phosphonomethyl)glycine on an acid equivalent basis.

322. The process as set forth in claim 321 wherein said aqueous feed mixture
contains at least about 35% by weight of a water-soluble salt of N-
(phosphonomethyl)iminodiacetic acid on an acid equivalent basis and said final
oxidation reaction mixture contains at least about 28% by weight of a water-soluble
5 salt of N-(phosphonomethyl)glycine on an acid equivalent basis.

323. The process as set forth in claim 320 wherein a final oxidation reaction is
concentrated by removal of water therefrom.

324. The process as set forth in claim 323 wherein said final reaction mixture
is introduced into a flash evaporation zone wherein the pressure is lower than the
vapor pressure of said final oxidation mixture at the temperature at which it exits said
primary reactor or said secondary reaction system.

325. The process as set forth in claim 323 wherein removal of water from said
final oxidation reaction product produces a concentrated solution containing at least
about 40% by weight of a water-soluble salt of N-(phosphonomethyl)glycine on an
acid equivalent basis.

326. The process as set forth in claim 325 wherein removal of water from said
final oxidation reaction product produces a concentrated solution containing at least
about 40% by weight of a water-soluble salt of N-(phosphonomethyl)glycine on an
acid equivalent basis.

327. The process as set forth in claim 315 wherein the temperature of said
liquid phase exit stream from said primary reaction zone is maintained below a

reference autogenous adiabatic reaction temperature that would result from absorption by said primary reaction mixture of the heat of reaction generated in said primary 5 reaction zone in the absence of any measure to maintain a lower exit temperature.

328. The process as set forth in claim 327 wherein maintaining the temperature of said liquid phase exit stream below said reference temperature comprises cooling of said fixed bed by indirect transfer of heat to a cooling fluid comprising a heat transfer or process fluid flowing through a conduit within or in 5 contact with said bed.

329. The process as set forth in claim 328 wherein said fixed bed is disposed within the shell or tube side of a shell and tube heat exchanger, said cooling fluid being passed through the other side of the exchanger.

330. The process as set forth in claim 329 wherein said fixed bed comprises multiple component beds separately disposed in the tubes of a shell and tube heat exchanger, said aqueous feed mixture and oxidant being distributed among said component beds for conversion therein of said N-(phosphonomethyl)iminodiacetic acid substrate to said N-(phosphonomethyl)glycine product, said cooling fluid flowing 5 through the shell side of said heat exchanger.

331. The process as set forth in claim 329 wherein said fixed bed is contained within the shell of a shell and tube heat exchanger,

332. The process as set forth in claim 327 wherein said fixed bed comprises a noble metal on carbon catalyst, and the liquid phase reacting mixture passes in substantially plug flow through said fixed bed within said heat exchanger, thereby promoting oxidation of by-product formaldehyde and/or formic acid therein.

333. The process as set forth in claim 327 wherein maintaining the temperature of said liquid phase exiting said bed below said reference temperature comprises introducing into said bed a recirculation fraction comprising N-(phosphonomethyl)glycine produced in the reaction wherein said recirculation fraction has been cooled externally of said fixed bed, said liquid phase feed stream comprising said aqueous feed mixture and said recirculation fraction.

334. The process as set forth in claim 333 comprising:
dividing the liquid phase exit stream into a primary product fraction and a primary reactor circulation fraction;
passing the liquid phase exit stream or the primary reactor recirculation fraction through a heat exchanger for removal of heat of oxidation of the N-(phosphonomethyl)iminodiacetic acid substrate; and
returning the primary reactor recirculation fraction to the primary oxidation reaction zone.

335. The process as set forth in claim 334 wherein said primary reaction mixture is passed through said heat exchanger before said primary reaction mixture is divided.

336. The process as set forth in claim 315 wherein said catalyst comprises a platinum on carbon catalyst comprising not greater than 3% platinum on a total catalyst basis.

337. A continuous process for the catalytic oxidation of an N-(phosphonomethyl)iminodiacetic acid substrate to produce an N-(phosphonomethyl)glycine product, comprising:

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- introducing a first component feed stream comprising an N-(phosphonomethyl)iminodiacetic acid substrate into the first of a series of continuous reaction zones, each of said series of reaction zones comprising an oxidation catalyst; introducing an oxidant into said first of said series of reaction zones; catalytically oxidizing said substrate in said first reaction zone to produce an intermediate reaction mixture stream containing N-(phosphonomethyl)glycine product;
- transferring the intermediate reaction mixture exiting said first reaction zone to the second of said series of reaction zones; catalytically oxidizing said substrate in each of said series of reaction zones; withdrawing an intermediate reaction mixture from each of said reaction zones;
- introducing into each succeeding reaction zone the intermediate reaction mixture produced in the preceding reaction zone; introducing an additional component feed stream into each of one or more of said reaction zones succeeding said first reaction zone in said series, each said additional feed stream comprising an N-(phosphonomethyl)iminodiacetic acid substrate;
- introducing an oxidant into one or more said reaction zones succeeding said first reaction zone in said series; and withdrawing a final reaction product from the last in said series of reaction zones.

337. A process as set forth in claim 336 wherein an additional component feed stream comprising an N-(phosphonomethyl)-iminodiacetic acid substrate is introduced into each of said series of reaction zones.

338. A process as set forth in claim 337 wherein an oxidant into each of said series of reaction zones.

339. A process as set forth in claim 338 comprising at least three continuous reaction zones in said series.

340. A process as set forth in claim 336 wherein one or more of said additional component feed streams contains solid N-(phosphonomethyl)iminodiacetic acid substrate.

341. A process as set forth in claim 336 wherein said N-(phosphonomethyl)iminodiacetic acid substrate comprises a water-soluble salt of N-(phosphonomethyl)iminodiacetic acid and the average concentration of said salt among said component feed solutions is such that said final oxidation reaction mixture contains at least about 10% by weight of a water-soluble salt of N-(phosphonomethyl)glycine on an acid equivalent basis.
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342. A process as set forth in claim 341 wherein said average concentration of said salt in said component feed solutions is such that final oxidation reaction mixture contains at least about 20% by weight of a water-soluble salt of N-(phosphonomethyl)glycine on an acid equivalent basis.

343. A process as set forth in claim 342 wherein said average concentration of said salt in said component feed solutions is such that final oxidation reaction mixture contains at least about 28% by weight of a water-soluble salt of N-(phosphonomethyl)glycine on an acid equivalent basis.

344. A process as set forth in claim 340 wherein a final oxidation reaction is concentrated by removal of water therefrom.

345. A process as set forth in claim 344 wherein said final reaction mixture is introduced into a flash evaporation zone wherein the pressure is lower than the vapor

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pressure of said final oxidation mixture at the temperature at which it exits said primary reactor or said secondary reaction system.

346. A process as set forth in claim 344 wherein removal of water from said final oxidation reaction product produces a concentrated solution containing at least about 40% by weight of a water-soluble salt of N-(phosphonomethyl)glycine on an acid equivalent basis.

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